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Synergistic Effect of Solvent Extraction in Zinc β -Diketone-TOPO System : Influence of Terminal Group of β -Diketones (Physical and Inorganic Chemistry)

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Synergistic Effect of Solvent Extraction in Zinc β -Diketone-TOPO System

Influence of Terminal Group of β -Diketones

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The influence of terminal of β -diketone on the synergistic effect was studied for Zn β -diketone-TOPO system. Acetylacetone (AA), pivaloylacetone (PvA), dipropionylmethane (DPrM), diisobutylmethane (DIBM), benzoylacetone (BzA), dibenzoylmethane (DBM), trifluoroacetylacetone (TAA), benzoyltrifluoroacetone (BFA), thenoyltrifluoroacetone (TTA) and ethylbenzoyl acetate (EtBzAc) were employed as the chelating reagent. The stability constant of the TOPO adducts increased in the sequence,



The high stability of the adducts containing CF_3 group may be attributed to the strong electron withdraw of CF_3 group which caused low electron density surroundings of the central metal ion.

INTRODUCTION

Recently, the synergistic effect in the solvent extraction has been appreciated as a weighty problem, and many valuable investigations have been performed especially in the system of metal- β -diketone-some organophosphorus compounds^{1)~4)}. The mechanism of the synergism was understood as the adducts formation between metal β -diketonate and neutral ligand, and the stability constants of several adduct were also obtained^{5)~9)}.

In the authors' laboratory, the systematic study is being carried: In previous paper, the synergistic effect of some oxygen- or nitrogen-containing Lewis bases was described for europium-benzoyltrifluoroacetone system,¹⁰⁾ and the effect of the central metal ion was studied and presented the relationship between the ionic radius of rare earth elements and the stability constant of the adducts of their benzoyltrifluoroacetone chelates with *n*-hexyl alcohol, tri-*n*-butyl phosphate (TBP) and tri-*n*-octylphosphine oxide (TOPO)¹¹⁾.

In the present research, the effect of the terminal group of β -diketone was investigated for zinc- β -diketone-TOPO system. The extraction constant of the zinc chelates and the stability constant of the adducts were obtained by using acetylacetone, pivaloylacetone, dipropionylmethane, diisobutylmethane, benzoylacetone, dibenzoylmethane, trifluoroacetylacetone, thenoyltrifluoroacetone and ethylbenzoyl acetate. These β -diketones might be classified into three groups;

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
CH_3 -containing, C_6H_5 -containing and CF_3 -containing groups. The influence on the synergism increased in the sequence from the former group to the latter one.

EXPERIMENTAL

Apparatus — Radioactivity measurements were made with a TEN NaI (44.5 mm in dia. \times 50.8 mm) well-type scintillation counter, model PS-300, coupled with a scaler, model SA-230. A Hitachi-Horiba pH meter, model M-4, was used for the pH measurements.

Materials — Radioisotope, zinc-65 was obtained from ORNL, USA, as chloride, in hydrochloric acid. It was diluted with 0.01 *M* perchloric acid to give a solution of about $1\mu\text{Ci/ml}$. Pivaloylacetone (PvA), dipropionylmethane (DPrM) and diisobutyrylmethane (DIBM) were synthesized by the acylation of methyl ketones by means of sodium amide^{1,2)}. The boiling points of the purified substances were 66–67°C/17 mmHg, 65–66°C/20 mmHg and 77–78°C/30 mmHg, respectively. Acetylacetone (AA), trifluoroacetylacetone (TAA), benzoylacetone (BzA), benzoyltrifluoroacetone (BFA), dibenzoylmethane (DBM), thenoyltrifluoroacetone (TTA) and tri-*n*-octylphosphine oxide (TOPO) were supplied from the Dojindo Co. Ltd., Research Laboratory. These reagents were used without the purification, except AA and TAA, which were distilled before the employment. Ethylbenzoyl acetate (EtBzAc) and all other reagents were of the reagent grade materials. β -Diketones are shown in Table 1.

Table 1. β -Diketones.

β -Diketone	R_1	R_2
Acetylacetone (AA)	CH_3	CH_3
Pivaloylacetone (PvA)	$(\text{CH}_3)_3\text{C}$	CH_3
Dipropionylacetone (DPrM)	C_2H_5	C_2H_5
Diisobutyrylmethane (DIBM)	$(\text{CH}_3)_2\text{CH}$	$(\text{CH}_3)_2\text{CH}$
Benzoylacetone (BzA)	C_6H_5	CH_3
Dibenzoylmethane (DBM)	C_6H_5	C_6H_5
Trifluoroacetylacetone (TAA)	CF_3	CH_3
Benzoyltrifluoroacetone (BFA)	C_6H_5	CF_3
Thenoyltrifluoroacetone (TTA)		CF_3
Ethylbenzoyl acetate (EtBzAc)	C_6H_5	$\text{C}_2\text{H}_5\text{O}$

Procedure — Partition procedure was almost the same as previously described^{10,11)}. Five milliliters of aqueous solution and the equal volume of organic solution were taken in a glass stoppered vessel, and shaken for one hour in a thermostat regulated at $20 \pm 1^\circ\text{C}$. Aqueous solution contained ^{65}Zn solution (1 mL), sodium perchlorate (0.1 *M*) and acetate buffer (0.01 *M*) and is adjusted to a desired pH. Organic solution contained β -diketone (0.05 *M* or 0.1 *M*) and TOPO in benzene. After

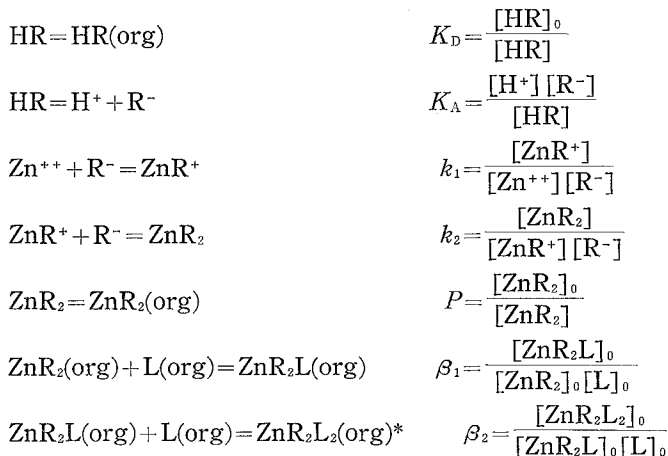
centrifugation, 1 ml of each of the two phases was pipetted into polyethylene counting tubes (14 mm in dia.), and gamma-activities were counted with the NaI scintillation counter. The pH value of the aqueous phase was again measured, which was used for plotting the distribution curve.

THEORETICAL

The distribution ratio, D , of zinc is calculated by the equation,

$$D = \frac{\gamma\text{-count rate per ml of the organic phase}}{\gamma\text{-count rate per ml of the aqueous phase}} \quad (1)$$

When zinc ion reacts with a β -diketone to form the β -diketonates, of which the uncharged chelate is extracted into organic phase and reacts with TOPO, if present, to produce the chelate adducts, the partitions and the reactions are expressed as follows:



where $[\]$ and $[\]_0$ designate the concentration in aqueous phase and organic phase; HR and L, β -diketone and TOPO, respectively.

The distribution ratios, D (in the absence of TOPO) and D' (in the presence of TOPO) can be given by the equations (2) and (3), if the concentration of zinc can be neglected in comparison with total concentration of the β -diketone; the contribution of the hydroxycomplexes and the acetate complexes are negligible; and the presence of TOPO does not give any change in the distribution of the β -diketone.

$$D = \frac{p \cdot k_1 \cdot k_2 [\text{R}^-]^2}{1 + k_1 [\text{R}^-] + k_1 \cdot k_2 [\text{R}^-]^2} \quad (2)$$

$$D' = \frac{p \cdot k_1 \cdot k_2 [\text{R}^-]^2 (1 + \beta_1 [\text{L}]_0)^*}{1 + k_1 [\text{R}^-] + k_1 \cdot k_2 [\text{R}^-]^2} \quad (3)$$

and at a definite pH,

$$D'/D = 1 + \beta_1 [\text{L}]_0 \quad (4)$$

or

$$\log D'/D = \log(1 + \beta_1 [\text{L}]_0) \quad (4')$$

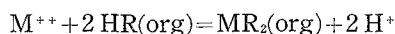
* The formation of the secondary adduct was not observed in this research.

Here, again assuming that free metal ion is a predominant species in the aqueous phase, the equation (2) may be reduced to the equations (5) and (5)'.

$$D = p \cdot k_1 \cdot k_2 \left(\frac{K_A [\text{HR}]_0}{K_D [\text{H}^+]} \right)^2 = K \frac{[\text{HR}]_0^2}{[\text{H}^+]^2} \quad (5)$$

$$\log D = \log K + 2 \log [\text{HR}]_0 + 2 \text{ pH} \quad (5)'$$

where K , the extraction constant, is an equilibrium constant of the following reaction:



RESULTS AND DISCUSSION

The $\log D$ vs. pH plots are shown in Figs. 1~3. From the equation (5)', it is expected that the plots should be straight line showing a slope of +2, if the $[\text{HR}]_0$ value is nearly constant in the pH region studied: This might be true, when the

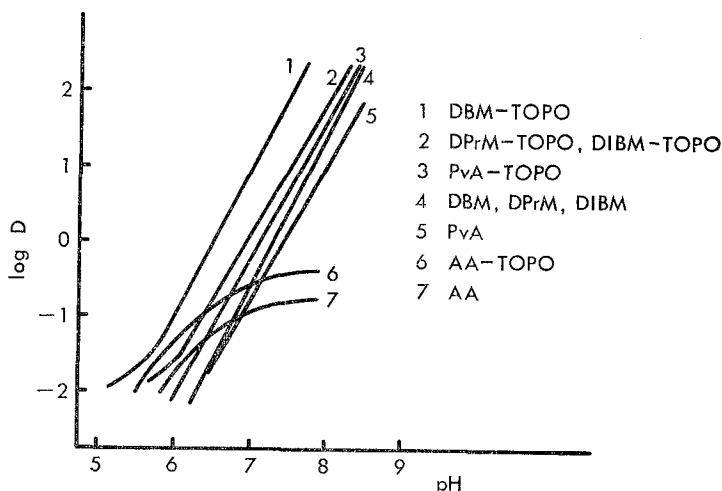


Fig. 1. Plot of $\log D$ vs. pH.
AA, DPrM and PvA = 0.1 M, DIBM = 0.05 M, TOPO = 10^{-3} M.

K_D value of the β -diketone is fairly high, but all the pH values studied are lower than $\text{p}K_A$, or when the highest pH value is about one unit lower than $\text{p}K_A$. For PvA, DPrM, DIBM, BzA, DBM, BFA and TTA, the slopes are approximately 2. However, it is somewhat smaller for EtBzAc, and the straight lines can not be obtained for AA and TAA. The deviation from the theoretical curves may be principally due to the partition of the uncharged chelate into the aqueous phase, because the assumption described just above is fulfilled, except in the case of the TAA extraction. In the TAA extraction without TOPO, not only the K_D value is rather low (≈ 1.2) but also the pH range covers the $\text{p}K_A$ (6.3), and therefore the $[\text{HR}]_0$ value can not be kept at constant. The fact may be the reason for the phenomena that the plot obtained in absence of TOPO shows a plateau above pH 6.3, while it becomes a straight line having a slope of 2 in the lower pH region by the addition of TOPO. The latter plot also deviates downwards near $\log D = 1$,

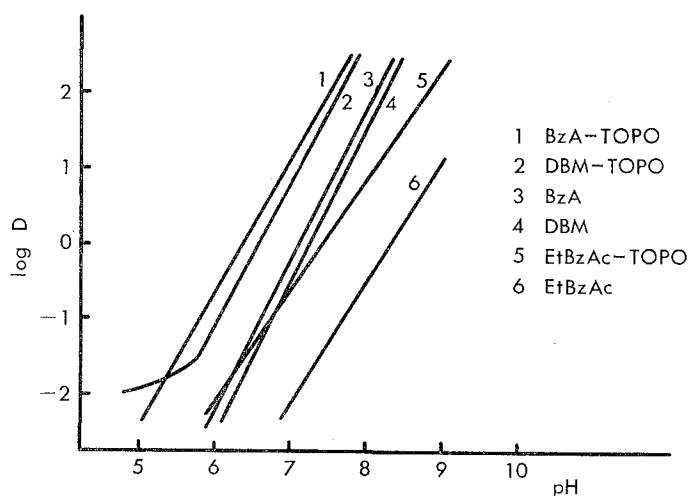


Fig. 2. Plot of $\log D$ vs. pH.
BzA, DBM and EtBzAc = $0.05 M$, TOPO = $10^{-3} M$.

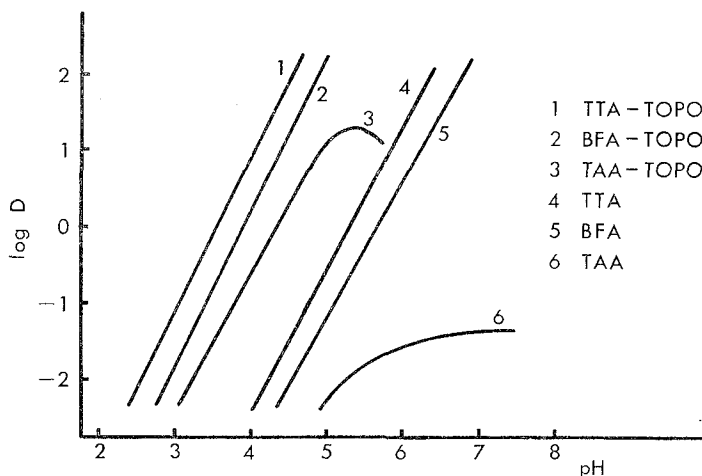


Fig. 3. Plot of $\log D$ vs. pH.
TTA, BFA and TAA = $0.05 M$, TOPO = $10^{-3} M$.

and this event is probably again owing to the partition of zinc bis-TAA chelate in aqueous phase.

The extraction constants were obtained by the equation (5)' for these zinc- β -diketone systems, except that for AA, TAA and EtBzA ones, and the results are summarized in Table 2.

Figures 4~13 show the plots of $\log D'/D$ vs. $\log [L]_0$, from which the stability constant of the adducts, β_1 , can be obtained. As seen in the figures, the asymptotes of the plot at infinite $[L]_0$ value have a slope of 1. This first-order dependency on the logarithmic TOPO concentration indicates the formation of the adduct with one mole of TOPO, such as $ZnR_2 \cdot TOPO$.

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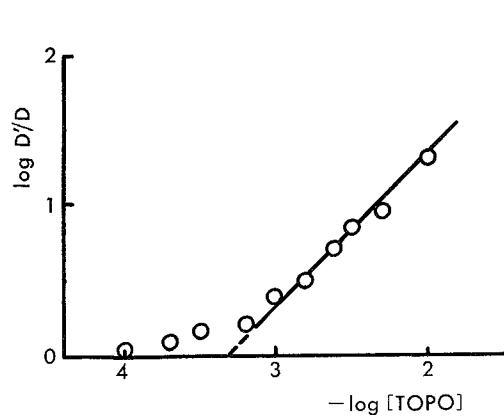


Fig. 4. 0.1 M AA-TOPO system. pH 6.0.

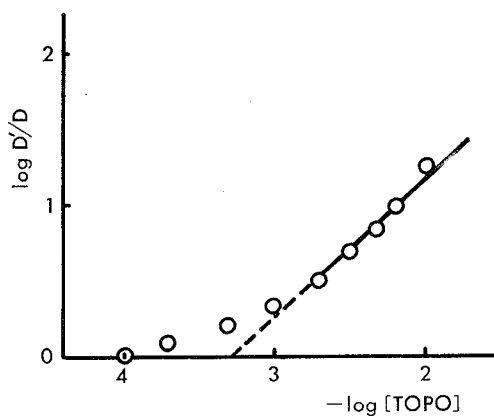


Fig. 5. 0.05 M DIBM-TOTO system. pH 6.5.

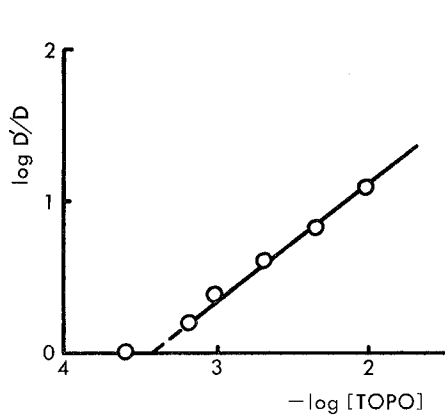


Fig. 6. 0.1 M DPrM-TOPO system. pH 6.5.

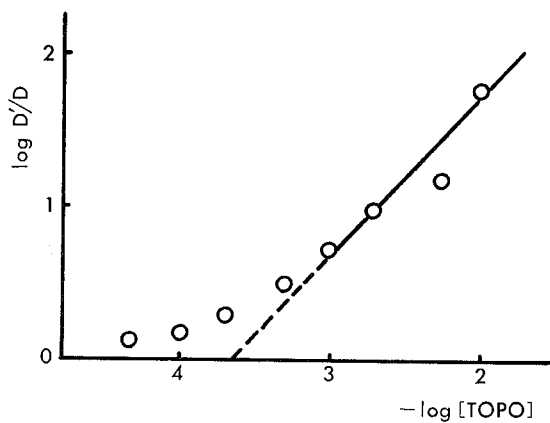


Fig. 7. 0.1 M PvA-TOPO system. pH 6.5.

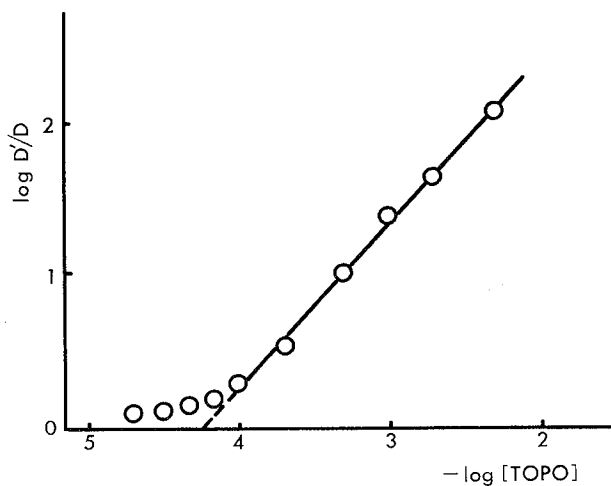


Fig. 8. 0.05 M BzA-TOPO system. pH 6.0.

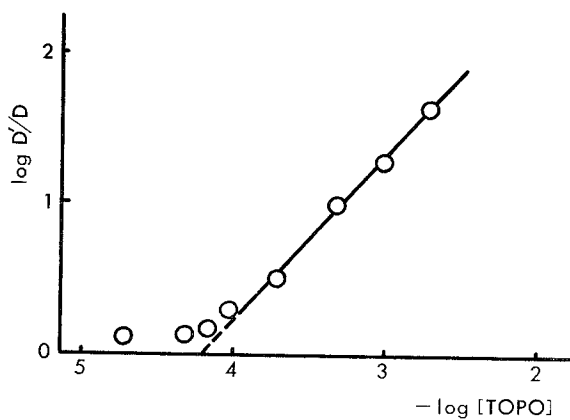


Fig. 9. 0.05 M EtBzAc-TOPO system. pH 7.0.

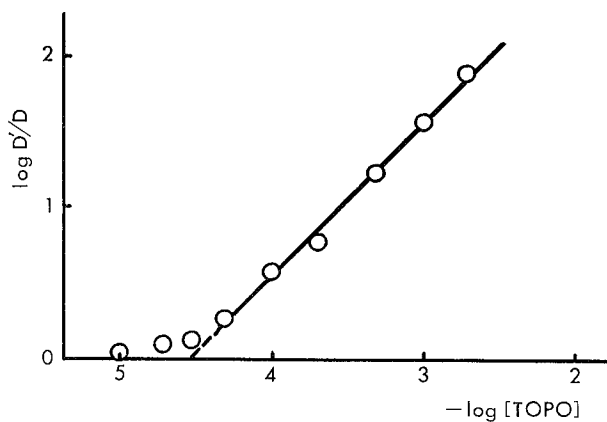


Fig. 10. 0.05 M DBM-TOPO system. pH 6.5.

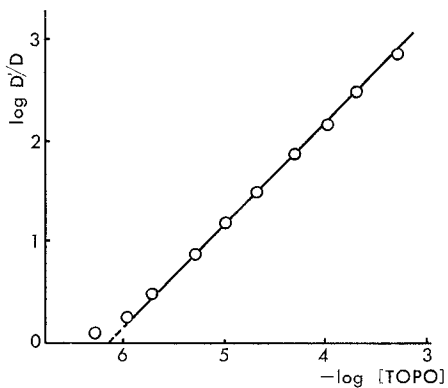


Fig. 11. 0.05 M TTA-TOPO system. pH 4.5.

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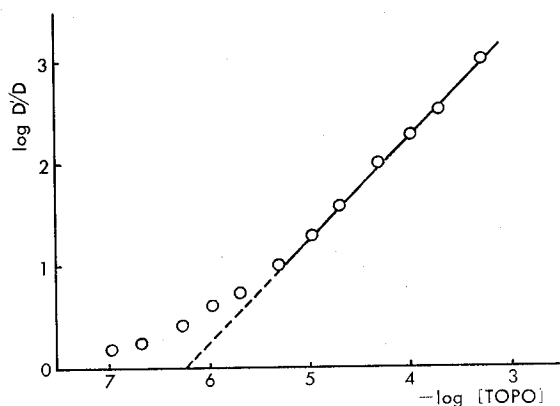


Fig. 12. 0.05 M BFA-TOPO system. pH 4.5.

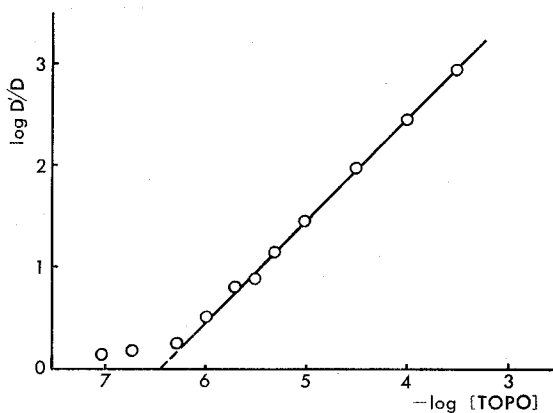


Fig. 13. 0.05 M TAA-TOPO system. pH 5.0.

Table 2. Extraction constant of chelates and stability constant of adducts.

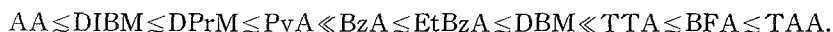
β -Diketone	$\log K$	$\log \beta_1$
AA	—	3.30*
DIBM	-11.68	3.35
DPrM	-11.27	3.42
PvA	-11.73	3.60
BzA	-11.54	4.16
DBM	-11.86	4.51
TTA	-7.95	6.17
BFA	-8.71	6.24
TAA	—	6.45*
EtBzAc	—	4.20*

* These values are inaccurate, because the $\log D$ vs. pH plot obtained in the absence of TOPO, much deviates from the theoretical curve.

The stability constants were determined by using the asymptote as

$$\log \beta_1 = -(\log [L]_0)_{\log D'/D=0}$$

and the results are summarized in Table 2. The stability constant of the adducts rises in the following order of β -diketone:



The order reveals the influence of terminal group of β -diketone on the synergistic effect. β -Diketone may be classified into three groups and the influence on the synergistic effect increases in the following sequence:

alkyl group < aromatic group < fluorine-containing group

The similar tendency was also observed in the lutetium(III)- β -diketone-TOPO system¹³⁾.

The higher stability of the adducts containing CF_3 group may be explained by the concept that the CF_3 radical strongly withdraws electrons from the surroundings of the coordination bond between zinc ion and the β -diketone, and thus enhances the ability to interact with further ligand such as TOPO. The stability constants of the adducts possessing phenyl group, are somewhat larger than that with methyl group. The phenomenon may be partly attributed to the resonance effect or the interaction of π -electron of aromatic group with that of chelate ring, which may lower the chelate bond between metal and diketone.

Recently, Wang and his co-workers¹⁴⁾ have reported the destruction of synergism in zinc-TTA-TOPO and zinc-hexafluoroacetylacetone-TOPO systems. In the present experiment, however, the concentration of TOPO is less than $10^{-3}M$, and such destruction was not observed.

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